

III.B.5 Diesel Plasma Reformer

Objectives

- Perform fundamental research in developing non-thermal plasma technology using model fuels.
- Optimize the plasma reactor's operating parameters for increased synthesis gas (syngas) yield and methane content in the reformat.
- Conduct validation tests for converting the organic sulfur compounds in diesel fuel to hydrogen.

Approach

- Determine the effect of plasma reactor type, residence time, applied power, and carrier gas on diesel conversion.
- Determine the sulfur conversion using optimized reactor conditions.

Accomplishments

- Obtained a three-fold increase in fuel conversion using a plasma reformer.
- Obtained a six-fold increase in hydrogen sulfide (H_2S) concentration in the reformer effluent gas stream.

Future Directions

- Maximize the fuel conversion in the plasma reformer.
- Maximize the sulfur conversion to H_2S in the plasma reformer.

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Introduction

The Solid State Energy Conversion Alliance has targeted Class 8 diesel trucks as a strong early market for 3 to 5 kW solid oxide fuel cell (SOFC) auxiliary power units (APUs). In order to make these units commercially viable by 2010, however, a breakthrough technology is required for processing liquid diesel fuel into a fuel cell grade feed. Our goal in this project is to develop an innovative fuel processing/desulfurization technology, based on the application of silent discharge plasma.

Various catalytic technologies are under consideration for the reforming of diesel fuel. These processes include auto-thermal reforming (ATR), catalytic partial oxidation (CPOx) and steam reforming (SR) [1]. Catalytic steam reforming is the conventional method for converting heavy petroleum-based distillates to a methane-rich gas. However, the reforming and fuel cell catalysts are highly prone to poisoning by the organic sulfurous compounds found in the distillate fuel [2].

Figure 1 shows a schematic of the proposed fuel processing system integrated with a SOFC APU. Diesel fuel and water are vaporized, and sent to the plasma reactor. The plasma reactor converts the diesel fuel to hydrogen, methane and light hydrocarbons. The sulfur compounds in diesel fuel are also converted to hydrogen sulfide in the plasma reactor, and then absorbed in a ZnO bed. The plasma reforming system has a number of key benefits when compared to conventional catalytic fuel processing systems: it is compact and desulfurization

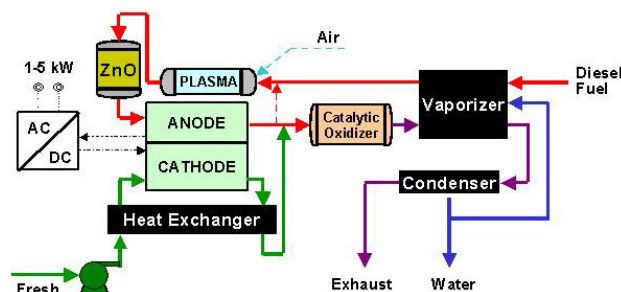


FIGURE 1. SOFC APU Plasma Reformer and ZnO Desulfurization Unit Schematic

and reforming are combined in one reactor. There are no catalysts, therefore reaction rates are not limited by catalyst active surface area. Reliability is increased with no deactivation due to sulfur. There is also the cost consideration; cost is reduced since there are no precious metals. Coking of the diesel fuel is an issue with conventional catalytic technologies but may be unlikely in the plasma reactor due to the presence of steam and the absence of catalytic surfaces.

The term “plasma” is defined as a region in space that has an equal number of positively charged ions and negatively charged electrons. In a non-thermal plasma, energy is channeled into the electrons which may reach temperatures in the range of tens to thousands Kelvin, while the ions and neutrals remain at nearly room temperature. The ions that are created in the plasma region are extremely reactive, and may form intermediate species with diesel fuel in a fashion similar to conventional catalysis. The goal of this project is to optimize the plasma operating conditions to achieve conversion of diesel fuel into a high methane content syngas and to also convert the organic sulfur compounds to H_2S .

Approach

Fundamental research is required to gain an insight into how plasma affects diesel fuel. Parametric tests were conducted to optimize diesel fuel conversion to methane, hydrogen and carbon oxides. The effect of plasma reactor design, residence time, feed composition and power input were quantified in terms of fuel conversion. The fuel conversion was determined via a carbon balance based on the chromatographic analysis of the exit gas stream. The main goal of the parametric study is to increase the concentration of methane in the exhaust stream as polymerizing or cracking the fuel could cause an increase in hydrogen concentration. A “non-reactive” carrier gas with a known flow was used to quantify the results.

Results

The parametric tests of the plasma reformer were conducted using dodecane, a sulfur-free model fuel to simulate diesel fuel. The purpose of using the model fuel was to be able to analyze the data with a greater degree of accuracy. The goal of this study was to investigate how the external system parameters affect the reformation process in the plasma reactor. We investigated the effect of total flow rate, steam to carbon ratio, and power input on the performance of the plasma reactor.

Of all the parameters tested, changing the steam to carbon ratio had the greatest effect on fuel conversion to methane. Fuel conversion and methane production

doubled when the steam to carbon ratio also doubled. The power output of the plasma was also investigated and found to have little effect on conversion rate when the power output tripled (from 100 W to 300 W).

The effect of these parameters on dodecane conversion was considered low, and therefore testing continued using JP-5. JP-5 contains aromatics that may provide active sites for the plasma, which the straight chain dodecane lacked. Here we looked at the carrier gas type and reactor design. We investigated three types of carrier gas: argon, nitrogen and air. We saw a three-fold increase in fuel conversion by introducing air as the carrier gas and conducting some partial oxidation in the plasma reformer. This is evidenced by an increase in carbon monoxide concentration using air (4.6%) compared with argon (0.6%). Runs conducted using air but without the plasma produced no carbon monoxide.

We also investigated plasma reactor designs. There were two types of reactors used in the testing: a coaxial dielectric barrier discharge (C-DBD) and a parallel-plate dielectric barrier discharge (PP-DBD). The coaxial dielectric barrier discharge reactor generates plasma in the space between an inner conductor rod (at high voltage) and an outer stainless steel tube (at ground potential). Vaporized fuel, steam and carrier gas flows in space between the inner rod and the tube. The plasma field is generated when high voltage AC power (up to 20 kV at 15–40 kHz) is applied to the inner rod.

The parallel-plate DBD reactor is shown in Figure 2. The stainless steel frame is the grounded electrode and a quartz plate forms the dielectric barrier. A removable copper plate is placed on top of the quartz and acts as the high potential conductor. The vaporized fuel, steam and carrier gas flows in a 1 mm field between the frame and the quartz plate.

Fuel conversion was comparable with either reactor. The parallel plate design easily lends itself to scale-up and is slightly more robust than the coaxial design.



FIGURE 2. Parallel-Plate Dielectric Barrier Discharge Device

The effectiveness of hydrogenating sulfur compounds in JP-5 was determined by measuring the sulfur compounds present in the gas stream. The JP-5 sulfur content was initially 1,100 ppm, much higher than the 50 ppm specification. The higher content was used to insure an appreciable concentration in the effluent. Sulfur content in the gas stream was determined using an Agilent 6890 gas chromatograph equipped with a thermal conductivity detector, a flame ionization detector and a Cavers 355 sulfur chemiluminescence detector. We investigated the effect of carrier gas type and plasma power on the concentrations of sulfur compounds in the reactor exhaust and the results are very encouraging. The total sulfur found in the stream containing the nitrogen purge is roughly equivalent to the sulfur associated with the converted fuel (1.2 ppm in the gas stream). By using air as the carrier gas, however, a 30-fold increase in the sulfur levels was realized (36.6 ppm). Partial oxidation is responsible for some of this increase, but the plasma contributes a 6-fold increase in sulfur levels compared to the no plasma run on air.

We also measured the sulfur content in the condensed liquid after the plasma reformer. The sulfur content dropped ~33% in the liquid, from 1,100 ppm to 740 ppm. This illustrates the possibility of using the plasma reformer as a pretreatment for sulfur containing fuel.

Conclusions and Future Directions

The results achieved under Phase 1 were very encouraging. This project showed a three-fold increase in fuel conversion using a plasma reformer and demonstrated the feasibility of sulfur removal by plasma. More work remains in fully developing the plasma reformer to become a stand alone component in reforming and desulfurizing diesel fuel. This future work is broken into six tasks, the first being overall project management. The second task is to develop a fuel delivery system that produces a steady flow of steam and vaporized diesel fuel to the plasma reactor with accuracy at both 1 kW and 5 kW feed levels. The third task focuses on optimizing a plasma reactor to achieve maximum hydrocarbon conversion efficiency and investigating the use of commercially available plasma systems. The fourth task will investigate plasma-assisted catalytic reforming. The fifth task encompasses both

additional parametric testing and computer modeling. Long-term testing is planned for the sixth task.

FY 2006 Publications/Presentations

1. Ghezal-Ayagh, H., Hunt, J., Ricatto, P., and Becker, K., "Diesel Reforming via Plasma", NETL SECA Fuel Processing Workshop, December 6, 2005.

References

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2. Krumpelt, M., Liu, D., and Sheen, S., "Diesel Reforming for Solid Oxide Fuel Cell Application," 2004 SECA Review Meeting, Boston, MA, May 11-13, 2004, <http://www.netl.doe.gov/publications/proceedings/04/seca-wrkshp/Argonne%20-%20Diesel%20Reforming%20-%20Krumpelt.pdf2>.
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